PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

4

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09K 5/04, C10M 107/32 — A1

(11) International Publication Number: WO 97/49781

(43) International Publication Date: 31 December 1997 (31.12.97)

(21) International Application Number: PCT/SE97/00935

(22) International Filing Date: 30 May 1997 (30.05.97)

(30) Priority Data:
9602464-1 24 June 1996 (24.06.96) SE

(71) Applicant *(for all designated States except US)*: PERSTORP AB [SE/SE]; S-284 80 Perstorp (SE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: SÖRENSEN, Kent [SE/SE]; Rönnvägen 4, S-284 35 Perstorp (SE). OGEMARK, Keith [SE/SE]; Stockholmsvägen 56, S-284 35 Perstorp (SE). SJÖGREEN, Carl-Axel [SE/SE]; Spjutserödsvägen 44, S-284 37 Perstorp (SE).

(74) Agent: STENBERG, Yngve; Perstorp AB, S-284 80 Perstorp (SE).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: A REFRIGERATION WORKING FLUID

(57) Abstract

A refrigeration working fluid comprising at least two components, of which at least one is a lubricant comprising at least one chain terminated dendritic or hyperbranched macromolecule and at least one is a refrigerant. The dendritic or hyperbranched macromolecule is composed of a monomeric or polymeric nucleus having at least one reactive epoxide, hydroxyl, carboxyl or anhydride group to which 1-100, preferably 1-20, generations of at least one monomeric or polymeric chain extender are added, which chain extender has at least one reactive hydroxyl group and at least one reactive carboxyl or is an inner ether of such a compound. A dendritic or hyperbranched macromolecule wherein terminal functions substantially are hydroxyl or carboxyl groups is yielded, which macromolecule completely or partially is chain terminated by at least one chain stopper being a saturated or unsaturated, linear or branched aliphatic carboxylic acid or anhydride or a saturated or unsaturated, linear or branched aliphatic alcohol or ether alcohol. The refrigerant comprises at least one halocarbon, such as a fluorocarbon or a chlorofluorocarbon.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

A REFRIGERATION WORKING FLUID

The present invention relates to a refrigeration working fluid comprising at least two components, whereby at least one is a lubricant comprising at least one completely or partly chain terminated dendritic or hyperbranched macromolecule of polyester type and at least one is a halocarbon refrigerant. The invention also refers to said lubricant.

Refrigeration systems such as refrigerators, freezers, air conditioners, heat pumps and the like normally include a circulating and heat transferring refrigerant. Refrigeration working fluids comprising normally used refrigerants, such as halocarbons, require a lubricant being compatible and miscible within a wide range of temperatures with said refrigerant so that moving parts in the system are properly lubricated. The properties and performances of halocarbon refrigerant fluids are well known and so is the environmental effects of those containing chlorine, which refrigerants presently to an increasing extent are replaced by substantially chlorine free compounds such as fluorocarbons. Ester and polyester based synthetic lubricants are also well known products and to a high extent used as lubricants in said systems. Many of the presently used lubricants, mineral based as well as said synthetic, exhibit an overall limited compatibility, miscibility and lubricating ability or most commonly a temperature dependent compatibility, miscibility and lubricating ability, especially at low temperatures and in combination with fluorocarbons.

The development efforts have for some time, more or less successfully, been focused on obtaining lubricating esters and polyesters being at all temperatures, especially at low temperatures, compatible and miscible with said refrigerants, especially fluorocarbon refrigerants. The lubricant must in order to provide proper lubrication over a wide range of temperatures have a low pour point and a high viscosity index. The problem of obtaining excellent miscibility at a very wide range of temperatures is most pronounced when chlorine containing halocarbon refrigerants and other heat transfer fluids are replaced with substantially chlorine free fluorocarbons. The fluorocarbons considered to be the most interesting and thus in focus of said development efforts are isomers of tetrafluoroethane, such as 1,1,1,2-tetrafluoroethane (commonly known as "Refrigerant 134a").

A synthetic lubricant must be formulated to provide required lubricating properties at a temperature interval as wide as possible. A well performing lubricant should to provide adequate lubricity have as invariable a viscosity as possible over a wide range of temperatures, however, yet being miscible with the refrigerant. Miscibility

at very low temperatures is especially difficult to obtain. An increased as well as a decreased viscosity normally negatively influence the lubricating ability of the ester or polyester. A lubricant must, furthermore, in most system exhibit a very high thermal stability and a high flash point.

Lubricating esters and polyesters frequently used in refrigeration systems and the like can suitably be exemplified by the general formula
$R^1 - (R^2)_{m-n} - (R^3)_n$ wherein
R^1 is a substituted or unsubstituted alkanyl, alkenyl, alkynyl, cycloalkanyl, cycloalkenyl, cycloalkynyl or aryl group normally derived from an alcohol, ether alcohol or carboxylic acid/anhydride, R^2 is HO or HOOC, R^3 is $\overset{\overset{O}{\|}}{C} - R^4$ or $O - R^4$,

wherein R^4 is a linear or branched alkanyl, alkenyl or alkenyl group, n and m are integers and at least 1, whereby m is the number of hydroxyl or carboxyl groups, in the alcohol, ether alcohol, carboxylic acid or anhydride from which R^1 is derived and is greater than or equal to n, whereby m-n can equals 0.

R^1 in above formula can of course also be derived from a hydroxyfunctional or carboxyfunctional ester, polyester, ether or polyether.

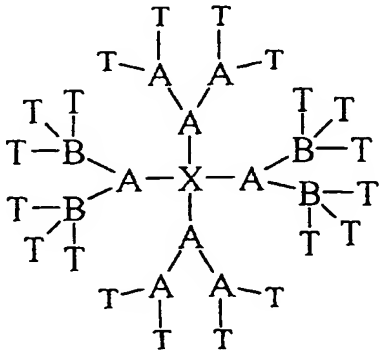
Various working fluids and lubricants comprising esters of above formula are disclosed and further discussed in a number of Patents and Patent Applications, including US 2,531,801, US 3,048,608, SE 358 407, WO 93/24597, WO 93/24596 and WO 93/11210.

Esters and polyesters as disclosed above have a viscosity index being highly dependent on such properties as the choice of raw materials, the molecular weight and the number of ester links. A drawback is that acceptable lubricating ability in most cases is limited to a more or less narrow range of temperatures. A further drawback is that most esters and polyesters have a limited thermal and/or chemical stability and resistance being highly dependent on for instance the choice of raw materials, the purity of said raw materials, the number of ester links and the acid and hydroxyl values. The solubility in fluorocarbons is for many esters and polyesters of above formula low in general or reduced at low or extremely low temperatures. The solubility in fluorocarbons is often judged by the temperature, the so called miscibility temperature, at which a solution of a compound such as said esters in above mentioned "Refrigerant 134a" separates. The miscibility

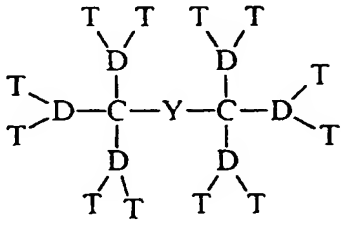
temperature of a 30% by weight solution of an ester as disclosed above is often to be found within the interval of +10°C and -30°C.

The present invention refers to a refrigeration working fluid comprising a lubricant having superior properties, especially at very low or very high temperatures. Said lubricant comprises at least one dendritic or hyperbranched macromolecule of polyester type, which macromolecule provides the superior properties. Dendritic and hyperbranched macromolecules (dendrimers) can generally be described as three dimensional highly branched molecules having a tree-like structure. Dendrimers are highly symmetric, while similar macromolecules designated as hyperbranched may to a certain degree hold an asymmetry, yet maintaining the highly branched tree-like structure. Dendrimers can be said to be monodisperse variations of hyperbranched macromolecules. Hyperbranched and dendritic macromolecules normally consist of an initiator or nucleus having one or more reactive sites and a number of surrounding branching layers, usually called generations, and optionally a layer of chain terminating molecules. A chain terminating molecule may either be monofunctional, such as a saturated or unsaturated carboxylic acid or alcohol, or provide the macromolecule with a suitable terminal functionality, such as hydroxyl, carboxyl, anhydride, epoxide, amine and/or alkenyl groups. Hyperbranched macromolecules of the polyester type give, due to the symmetrical or near symmetrical highly branched structure, in comparison to ordinary polyesters great advantages. Hyperbranched macromolecules exhibit especially in comparison to branched, but also linear, polyesters a low polydispersity. The structure of chain terminated hyperbranched or dendritic macromolecules having two chain extending generations can be illustrated by below schematically Formulas (I) and (II):

Formula (I)



Formula (II)



wherein X and Y each is an initiator or a nucleus, having four (X) and two (Y)

reactive sites; A, B, C and D each is a chain extender, having three (A and D) and four (B and C) reactive sites, each chain extender forming one generation in the macromolecule and wherein T is a chain terminating molecule.

The refrigeration working fluid of the present invention comprises at least two components, of which at least one is a lubricant comprising at least one completely or partly chain terminated dendritic or hyperbranched macromolecule of polyester type and at least one is a halocarbon refrigerant. The dendritic or hyperbranched macromolecule is composed of a monomeric or polymeric nucleus having at least one reactive epoxide, hydroxyl, carboxyl or anhydride group to which 1-100, preferably 1-20, generations of at least one monomeric or polymeric chain extender are added, which chain extender has at least one reactive hydroxyl group and at least one reactive carboxyl or is an inner ether of a compound having at least one hydroxyl and at least one carboxyl or anhydride group. A dendritic or hyperbranched macromolecule wherein terminal functions substantially are hydroxyl or carboxyl groups is thus yielded, which macromolecule then completely or partially chain terminated by at least one chain stopper, which chain stopper is a saturated or unsaturated, linear or branched aliphatic carboxylic acid or anhydride, a saturated or unsaturated, linear or branched aliphatic alcohol or ether alcohol and/or a lactone. The refrigerant of said fluid comprises at least one halocarbon, such a fluorocarbon or a chlorofluorocarbon.

A dendritic or hyperbranched macromolecule, in accordance with the present invention, exhibits excellent thermal stability and excellent solubility in fluorocarbons. Said dendritic or hyperbranched macromolecule exhibits due to its molecular structure high viscosities implying good lubricity at increased temperatures and excellent miscibility with halocarbons at low temperatures. The miscibility temperature is often less than -60°C. The thermal stability of the dendritic or hyperbranched macromolecules of the lubricant and the refrigeration working fluid of the present invention, is superior and often more than 80 minutes at 220°C according to DSC (Differential Scanning Colorimetry) determinations.

The dendritic or hyperbranched macromolecule comprises in preferred embodiments a nucleus selected among mono, di, tri or polyfunctional alcohols, reaction products between said alcohols and an alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide, or among mono, di, tri or polyfunctional epoxides, whereby yielding a dendritic or hyperbranched macromolecule wherein the terminal functions substantially are

hydroxyl groups. The most preferred alcohols can be exemplified by trimethylolpropane diallyl ether, pentaerythritol triallyl ether, glycerol diallyl ether, 5-ethyl-1,3-dioxane-5-methanol, 1,3-dioxane-5,5-dimethanol, ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, cyclohexane dimethanol, neopentyl glycol hydroxypivalate, neopentyl glycol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, pentanediol, trimethylolpropane monoallyl ether, glycerol monoallyl ether, glycerol, trimethylolpropane, trimethylolethane, ditrimethylolpropane, ditrimethylolethane, pentaerythritol, dipentaerythritol, tripentaerythritol or sorbitol and the likewise preferred epoxides by 1,2-epoxy-3-allyloxypropane, 1-allyloxy-2,3-epoxypropane, 1,2-epoxy-3-phenoxy-propane, 1-glycidyloxy-2- ethylhexane, bisphenol A-diglycidyl ether or reaction products thereof, diglycidyl terephthalate, epoxidised soybean fatty acid, epoxidised soybean oil, epoxidised polyvinyl alcohol or 3,4-epoxy-cyclohexyl-methyl-3,4-epoxy-cyclohexane carboxylate.

Reaction products of alcohols and alkylene oxides preferably include such compounds as ethoxylated and/or propoxylated glycerol, trimethylolpropane, trimethylolethane, ditrimethylolpropane, ditrimethylolethane, pentaerythritol and dipentaerythritol, but can also suitably include ethoxylated and/or propoxylated 1,3-dioxane alcohols, such as 5-ethyl-1,3-dioxane-5-methanol and 1,3-dioxane-5,5-dimethanol.

The chain extender of the dendritic or hyperbranched macromolecule in preferred embodiments a hydroxyfunctional carboxylic acid, such as 2,2-dimethylolpropionic acid, α,α-bis(hydroxymethyl)butyric acid, α,α,α-tris(hydroxymethyl)acetic acid, α,α-bis(hydroxymethyl)valeric acid, α,α-bis(hydroxymethyl)propionic acid, α,β-dihydroxypropionic acid, heptonic acid, citric acid, *d*- or *l*-tartaric acid, dihydroxymaloic acid, *d*-gluconic acid, hydroxyvaleric acid, hydroxypropionic acid. hydroxypivalic acid and/or most preferably any of the dihydroxyfunctional monocarboxylic acids included herein. Alternative embodiments of the dendritic or hyperbranched macromolecule comprises at least one α-phenylcarboxylic acid having at least two hydroxyl groups directly pendant to the phenyl ring, such as 3,5-dihydroxybenzoic acid. A chain extender may also be selected among lactones, which are inner ethers of hydroxyfunctional carboxylic acids. Lactones are most suitably exemplified by δ-valerolactone, β-propiolactone, ε-caprolactone and glycolide.

The chain termination is in preferred embodiments of the dendritic or hyperbranched macromolecule performed by adding to the terminal functions at least one chain stopper being a carboxylic acid, preferably a linear or branched aliphatic monobasic carboxylic acid. Said carboxylic acid is suitably selected from the group consisting of formic acid, acetic acid, propionic acid, isopropionic acid, butanoic acid; isobutanoic acid, valeric acid, isovaleric acid, hexanoic acid, isohexanoic acid, heptanoic acid; isoheptanoic acid; octanoic acid; isooctanoic acid, nonanoic acid, isononanoic acid, decanoic acid, isodecanoic acid, acrylic acid, methacrylic acid, crotonic acid, caproic acid, caprylic acid, capric acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, lignoceric acid, cerotic acid, montanoic acid, abietic acid, sorbinic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, erucic acid, benzoic acid, *p*-tert.butylbenzoic acid, soybean fatty acid, linseed fatty acid, castor fatty acid, dehydrated castor fatty acid, tall oil fatty acid, tung oil fatty acid, sunflower fatty acid, safflower fatty acid, tallow fatty acid and oiticica fatty acid and preferably from the group consisting of mono, di or trialkyl acetic acids, such as methylethylacetic acid. The carboxylic acid is most preferably selected among trimethylacetic acid; mono, di or trialkyl propionic acids, such as 2,2-dimethylpropionic acid; mono, di or trialkyl butanoic acids, such as 2-ethyl-2-methylbutanoic acid; mono, di or trialkyl hexanoic acids, such as 2-methylhexanoic acid 2-ethylhexanoic acid, dimethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and/or alkylbenzoic acids, such as *p*-tert.butylbenzoic acid.

The nucleus can, in alternative embodiments of the dendritic or hyperbranched macromolecule included in the refrigeration working fluid according to the present invention, be a carboxylic acid or anhydride, preferably a di, tri or polyfunctional carboxylic acid, or where applicable an anhydride thereof, having 3-24 carbon atoms, whereby a dendritic or hyperbranched macromolecule wherein said terminal functions substantially are hydroxyl groups is yielded. The chain stopper in such embodiments is preferably a linear of branched aliphatic or cycloaliphatic alcohol or ether alcohol having 1-30, such as 10-20, carbon atoms, wherein one or more carbon atoms are alkanyl, alkenyl, alkynyl or aryl substituted. The alcohols is advantageously polyethoxylated or polypropoxylated. Some preferred alcohols can be exemplified by such monofunctional alcohols as propanols, butanols, pentanols, hexanols, heptanols, octanols, nonanols and dodecanol or by the monoalcohols 5-ethyl-1,3-dioxane-5-methanol, trimethylolpropane diallyl ether, pentaerythritol

triallyl ether, lauryl alcohol, palmityl alcohol, oleyl alcohol and/or ceryl alcohol, including ethoxylates and propoxylates thereof.

The refrigerant of the refrigeration working fluid of the present invention comprises in preferred embodiments at least one fluoroethane being a difluoroethane, such as 1,1-difluoroethane; a trifluoroethanes, such as 1,1,1-trifluoroethane; a tetrafluoroethane, such as 1,1,1,2-tetrafluoroethane; and/or a pentafluoroethane. The refrigerant can also be selected among most halocarbon refrigerants, including chlorine containing refrigerants such as the still commonly used trichlorofluoromethane and dichlorodifluoromethane.

An especially preferred embodiment of the present invention is a refrigeration working fluid, wherein

a) the dendritic or hyperbranched macromolecule is composed of
   i) a nucleus being a di, tri or polyfunctional alcohol of neopentyl structure or a reaction product between such an alcohol and ethylene and/or propylene oxide, yielding a dendritic or hyperbranched macromolecule wherein the terminal functions substantially are hydroxyl groups,
   ii) 1-5 generations of a chain extender being a dihydroxyfunctional monocarboxylic acid, preferably 2,2-dimethylolpropionic acid, and
   iii) a chain stopper being a linear or branched aliphatic saturated or unsaturated monocarboxylic acid having 1-24 carbon atoms, and wherein
b) the refrigerant is a tetrafluoroethane, preferably 1,1,1,2-tetrafluoroethane.

The most preferred embodiments of the invention all include a lubricant composition consisting of at least one dendritic or hyperbranched macromolecule as herein disclosed and in addition thereto at least one conventional ester or polyester, preferably of general formula

$R^1 - (R^2)_{m-n} - (R^3)_n$ wherein

R^1 is a substituted or unsubstituted alkanyl, alkenyl, alkynyl, cycloalkanyl, cycloalkenyl, cycloalkanyl or aryl group derived from an alcohol, ether alcohol or from a carboxylic acid or anhydride,

R^2 is HO or HOOC,

R^3 is $\overset{\overset{O}{\|}}{C} - R^4$ or $O - R^4$ wherein R^4 is linear or branched alkanyl, alkenyl or alkynyl

and wherein *n* and *m* are integers being at least 1, whereby *m* is greater than or equal to *n* and whereby *m-n* can equals 0.

A refrigeration working fluid comprises normally 1-60% by weight of the lubricant and 40-99% by weight of the halocarbon. The lubricant suitably comprises 1-80%, such as 1-10% or 5-50%, by weight of the dendritic or hyperbranched macromolecule and optionally in addition to said components at least one additive, such as a stabiliser, an antioxidant or the like.

These and other objects and the attendant advantages will be more fully understood from the following detailed description, taken in conjunction with embodiment Examples 1-5. While particular embodiments of the invention will be shown, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

Example 1: Preparation and chain termination of a 1 generation hyperbranched macromolecule, wherein the nucleus is neopentyl glycol, the chain extender 2,2-dimethylolpropionic acid and the chain stopper valeric acid.

Example 2: Preparation and chain termination of a 1 generation hyperbranched macromolecule, wherein the nucleus is neopentyl glycol, the chain extender 2,2-dimethylolpropionic acid and the chain stopper 3,5,5-trimethylhexanoic acid.

Example 3: Preparation and chain termination of a 1 generation hyperbranched macromolecule, wherein the nucleus is trimethylolpropane, the chain extender 2,2-dimethylolpropionic acid and the chain stopper valeric acid.

Example 4: Preparation and chain termination of a 2 generations hyperbranched macromolecule, wherein the nucleus is trimethylolpropane, the chain extender 2,2-dimethylolpropionic acid and the chain stopper valeric acid.

Example 5: Comparative Example related to a polyol ester known in the art to have good to excellent miscibility in fluorocarbons and to have good to excellent thermal stability.

The hyperbranched lubricants of Examples 1-4 and the ester of Example 5 are all evaluated for miscibility and miscibility temperature in a fluorocarbon refrigerant as well as thermal stability.

Example 1

Preparation and chain termination of a 1 generation hyperbranched macromolecule, wherein the nucleus is neopentyl glycol, the chain extender 2,2-dimethylol-propionic acid and the chain stopper valeric acid. The macromolecule is evaluated for miscibility and miscibility temperature in a fluorocarbon refrigerant as well as for thermal stability.

209.8 g (2.0 moles) of neopentyl glycol (Perstorp Polyols, Sweden), 544.8 g (4.0 moles) of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Polyols, Sweden), 23.0 g of heptane and 1.5 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer, cooler and water trap (Dean-Stark). The temperature was raised to 120°C, at which temperature esterification water was formed. The temperature was thereafter during 60 minutes raised to 140°C. The reaction was, under stirring, allowed to continue for 8 hours, after which time a vacuum of 10-20 mm Hg was applied for 30 minutes. Obtained product was now cooled to room temperature.

Obtained hyperbranched polyester exhibited the following properties:

Acid value, mg KOH/g:	5.4
Hydroxyl value, mg KOH/g:	667
Viscosity (Cone & Plate) at 100°C, mPas:	480
Calculated molecular weight, g/mole:	337

302.8 g (0.9 mole) of the hyperbranched polyester obtained above, 440.6 g (4.32 moles) of valeric acid, 37 g of heptane and 1.5 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer, cooler and water trap (Dean-Stark). The temperature was raised to 125°C, at which temperature esterification water was formed. The temperature was thereafter during 40 minutes raised to 150°C. The reaction was, under stirring, allowed to continue for 14 hours, after which time a vacuum of < 5 mm Hg was applied for 2 hours. Obtained product was now neutralised with $Ca(OH)_2$, filtered and cooled to room temperature.

Obtained hyperbranched lubricant exhibited the following properties:

Acid value, mg KOH/g:	0.08
Hydroxyl value, mg KOH/g:	5
Viscosity at 40°C, mPas:	63
Thermal stability, DSC 220°C, min:	> 80
Miscibility temperature, 30% in "134a", °C:	< -60

The hyperbranched lubricant was at temperatures above the miscibility temperature miscible with "Refrigerant 134a" in all proportions.

The miscibility temperature was determined as the temperature at which a 30% by weight solution of the hyperbranched lubricant in "Refrigerant 134a" (Solkan 134a, Solvay Fluor und Derivate GmbH, Germany) separates and thermal stability was determined by DSC (Differential Scanning Colorimetry) as minutes at 220°C. This is also valid for Examples 2-5 below.

Example 2

Preparation and chain termination of a 1 generation hyperbranched macromolecule, wherein the nucleus is neopentyl glycol, the chain extender 2,2-dimethylol-propionic acid and the chain stopper 3,5,5-trimethylhexanoic acid. The macromolecule is evaluated for miscibility and miscibility temperature in a fluorocarbon refrigerant as well as for thermal stability.

209.8 g (2.0 moles) of neopentyl glycol (Perstorp Polyols, Sweden), 544.5 g (4.0 moles) of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Polyols, Sweden), 23.0 g of heptane and 3.0 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer, cooler and water trap (Dean-Stark). The temperature was raised to 120°C, at which temperature esterification water was formed. The temperature was thereafter during 60 minutes raised to 140°C. The reaction was, under stirring, allowed to continue for 8 hours, after which time a vacuum of 10-20 mm Hg was applied for 30 minutes. Obtained product was now cooled to room temperature.

Obtained hyperbranched polyester exhibited the following properties:

Acid value, mg KOH/g:	5.4
Hydroxyl value, mg KOH/g:	667

Viscosity (Cone & Plate) at 100°C, mPas:	480
Calculated molecular weight, g/mole:	337

235.5 g (0.7 mole) of the hyperbranched polyester obtained above, 537.1 g (3.36 moles) of 3,5,5-trimethylhexanoic acid, 39.0 g of heptane and 1.5 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer, cooler and water trap (Dean-Stark). The temperature was raised to 140°C, at which temperature esterification water was formed. The temperature was thereafter during 2 hours raised to 150°C. The reaction was, under stirring, allowed to continue at 150°C for 6 hours, after which time the temperature was raised to 170°C and maintained for a further 8 hours. A vacuum of < 5 mm Hg was now applied for 2 hours. Obtained product was neutralised with $Ca(OH)_2$, filtered and cooled to room temperature.

Obtained hyperbranched lubricant exhibited the following properties:

Acid value, mg KOH/g:	0.06
Hydroxyl value, mg KOH/g:	2
Viscosity at 40°C, mPas:	310
Thermal stability, DSC 220°C, min:	> 80
Miscibility temperature, 30% in "134a", °C:	-35

The hyperbranched lubricant was at temperatures above the miscibility temperature miscible with "Refrigerant 134a" in all proportions.

Example 3

Preparation and chain termination of a 1 generation hyperbranched macromolecule, wherein the nucleus is trimethylolpropane, the chain extender 2,2-dimethylol-propionic acid and the chain stopper valeric acid. The macromolecule is evaluated for miscibility and miscibility temperature in a fluorocarbon refrigerant as well as for thermal stability.

175.2 g (1.3 moles) of trimethylolpropane (Perstorp Polyols, Sweden), 522.3 g (3.9 moles) of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Polyols, Sweden), 21.0 g of heptane and 2.8 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer,

cooler and water trap (Dean-Stark). The temperature was raised to 120°C, at which temperature esterification water was formed. The temperature was thereafter during 40 minutes raised to 140°C. The reaction was, under stirring, allowed to continue for 14 hours, after which time a vacuum of 10-20 mm Hg was applied for 30 minutes. Obtained product was now cooled to room temperature.

Obtained hyperbranched polyester exhibited the following properties:

Acid value, mg KOH/g:	1.4
Hydroxyl value, mg KOH/g:	698
Viscosity (Cone & Plate) at 125°C, mPas:	910
Calculated molecular weight, g/mole:	483

289.5 g (0.6 mole) of the hyperbranched polyester obtained above, 440.6 g (4.32 moles) of valeric acid, 37.0 g of heptane and 1.5 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer, cooler and water trap (Dean-Stark). The temperature was raised to 125°C, at which temperature esterification water was formed. The temperature was thereafter during 3.5 hours raised to 150°C. The reaction was, under stirring, allowed to continue at 150°C for 8 hours, after which time a vacuum of < 5 mm Hg was applied for 2 hours. Obtained product was now neutralised with $Ca(OH)_2$, filtered and cooled to room temperature.

Obtained hyperbranched lubricant exhibited the following properties:

Acid value, mg KOH/g:	0.01
Hydroxyl value, mg KOH/g:	3
Viscosity at 40°C, mPas:	265
Thermal stability, DSC 220°C, min:	60
Miscibility temperature, 30% in "134a", °C:	< -60

The hyperbranched lubricant was at temperatures above the miscibility temperature miscible with "Refrigerant 134a" in all proportions.

Example 4

Preparation and chain termination of a 2 generations hyperbranched macromolecule, wherein the nucleus is trimethylolpropane, the chain extender 2,2-dimethylolpropionic acid and the chain stopper valeric acid. The macromolecule is evaluated for miscibility and miscibility temperature in a fluorocarbon refrigerant as well as for thermal stability.

161.7 g (1.2 mole) of trimethylolpropane (Perstorp Polyols, Sweden), 493.9 g (3.6 moles) of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Polyols, Sweden) and 4.9 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, cooler and receiver. The temperature was raised to 140°C, at which temperature esterification water was formed. The temperature was maintained for 90 minutes. A vacuum of 30-50 mm Hg was now applied and the reaction allowed to continue at said vacuum and 140°C for a further 90 minutes. The vacuum was released and 987.8 g (7.2 moles) of 2,2-dimethylolpropionic acid and 9.9 g of *p*-toluenesulphonic acid were now during 15 minutes added to the reaction mixture. A vacuum of 30-50 mm Hg was applied when charged 2,2-dimethylolpropionic acid was dissolved. The reaction was now allowed to continue for a further 3.5 hours. Obtained product was thereafter cooled to room temperature.

Obtained hyperbranched polyester exhibited the following properties:

Acid value, mg KOH/g:	7.4
Hydroxyl value, mg KOH/g:	558
Viscosity (Cone & Plate) at 175°C, mPas:	450
Calculated molecular weight, g/mole:	1208

362.3 g (0.3 mole) of the hyperbranched polyester obtained above, 440.6 g (4.32 moles) of valeric acid, 40 g of heptane and 1.6 g of *p*-toluenesulphonic acid were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, nitrogen inlet, thermometer, cooler and water trap (Dean-Stark). The temperature was raised to 120°C, at which temperature esterification water was formed. The temperature was thereafter during 3.5 hours raised to 140°C. The reaction was, under stirring, allowed to continue at 140°C for 4 hours and thereafter raised to 150°C. The reaction was allowed to continue at 150°C for a further 8 hours, after

which time a vacuum of < 5 mm Hg was applied for 2 hours. Obtained product was now neutralised with $Ca(OH)_2$, filtered and cooled to room temperature.
Obtained hyperbranched lubricant exhibited the following properties:

Acid value, mg KOH/g:	0.1
Hydroxyl value, mg KOH/g:	5
Viscosity at 40°C, mPas:	1026
Thermal stability, DSC 220°C, min:	> 80
Miscibility temperature, 30% in "134a", °C:	-33

The hyperbranched lubricant was at temperatures above the miscibility temperature miscible with "Refrigerant 134a" in all proportions.

Example 5 (Comparative Example)

A polyol ester known in the art to exhibit good to excellent miscibility in fluorocarbons and to have good to excellent thermal stability was prepared and evaluated in the same way as the hyperbranched lubricants of Examples 1-4.

Ditrimethylolpropane was esterified with 3,5,5-trimethylhexanoic acid according to known esterification procedures to yield an ester having four ester links.

Obtained ester lubricant exhibited the following properties:

Acid value, mg KOH/g:	0.01
Hydroxyl value, mg KOH/g:	6
Viscosity at 40°C, mPas:	158
Thermal stability, DSC 220°C, min:	22
Miscibility temperature, 30% in "134a", °C:	-12

The lubricant was at temperatures above the miscibility temperature miscible with "Refrigerant 134a" in all proportions.

The lubricant of this Example, known in the art to have good or excellent properties, exhibits a substantially poorer thermal stability and a substantially higher miscibility temperature compared to the hyperbranched lubricants of Examples 1-4.

CLAIMS

1. A refrigeration working fluid
characterised in, that
the fluid comprises at least two components, of which at least one is a lubricant comprising at least one completely or partly chain terminated dendritic or hyperbranched macromolecule of polyester type and at least one is a refrigerant, whereby

   a) said dendritic or hyperbranched macromolecule is composed of a monomeric or polymeric nucleus having at least one reactive epoxide, hydroxyl, carboxyl or anhydride group to which 1-100, preferably 1-20, generations of at least one monomeric or polymeric chain extender are added, the chain extender being a compound having at least one reactive hydroxyl group and at least one reactive carboxyl or being an inner ether of such a compound, thus yielding a dendritic or hyperbranched macromolecule wherein terminal functions substantially are hydroxyl or carboxyl groups, which macromolecule is completely or partially chain terminated by at least one chain stopper, which chain stopper is a saturated or unsaturated, linear or branched aliphatic carboxylic acid or anhydride and/or saturated or unsaturated, linear or branched aliphatic alcohol or ether alcohol;
   and whereby
   b) said refrigerant comprises at least one halocarbon, such a fluorocarbon or a chlorofluorocarbon.

2. A refrigeration working fluid according to claim 1
characterised in, that
the nucleus of the dendritic or hyperbranched macromolecule is a mono, di, tri or polyfunctional alcohol, whereby a dendritic or hyperbranched macromolecule wherein said terminal functions substantially are hydroxyl groups is yielded.

3. A refrigeration working fluid according to claim 1
characterised in, that
the nucleus of the dendritic or hyperbranched macromolecule is a reaction product between a mono, di, tri or polyfunctional alcohol and an alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide and/or

phenylethylene oxide, whereby a dendritic or hyperbranched macromolecule wherein said terminal functions substantially are hydroxyl groups is yielded.

4. A refrigeration working fluid according to claim 2 or 3
characterised in, that
the mono, di, tri or polyfunctional alcohol is trimethylolpropane diallyl ether, pentaerythritol triallyl ether, glycerol diallyl ether, 5-ethyl-1,3-dioxane-5-methanol, 1,3-dioxane-5,5-dimethanol, ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, cyclohexane dimethanol, neopentyl glycol hydroxypivalate, neopentyl glycol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, pentanediol, trimethylolpropane monoallyl ether, glycerol monoallyl ether, glycerol, trimethylolpropane, trimethylolethane, ditrimethylolpropane, ditrimethylolethane, pentaerythritol, dipentaerythritol, tripentaerythritol or sorbitol.

5. A refrigeration working fluid according to claim 1
characterised in, that
the nucleus of the dendritic or hyperbranched macromolecule is a mono, di, tri or polyfunctional epoxide, whereby a dendritic or hyperbranched macromolecule wherein said terminal functions substantially are hydroxyl groups is yielded.

6. A refrigeration working fluid according to claim 5
characterised in, that
the epoxide is selected from the group consisting of 1,2-epoxy-3-allyloxypropane, 1-allyloxy-2,3-epoxypropane, 1,2-epoxy-3-phenoxypropane, 1-glycidyloxy-2-ethylhexane, bisphenol A-diglycidyl ether or a reaction product thereof, diglycidyl terephthalate, epoxidised soybean fatty acid, epoxidised soybean oil, epoxidised polyvinyl alcohol or 3,4-epoxy-cyclohexyl methyl-3,4-epoxy cyclohexane carboxylate.

7. A refrigeration working fluid according to any of the claims 1-6
characterised in, that
at least one chain extender in the dendritic or hyperbranched macromolecule is a hydroxyfunctional carboxylic acid.

8. A refrigeration working fluid according to claim 7
characterised in, that
the hydroxyfunctional carboxylic acid is 2,2-dimethylolpropionic acid, α,α-bis(hydroxymethyl)butyric acid, α,α,α-tris(hydroxymethyl)acetic acid, α,α-bis(hydroxymethyl)valeric acid, α,α-bis(hydroxymethyl)propionic acid, α,β-dihydroxypropionic acid, heptonic acid, citric acid, *d*- or *l*-tartaric acid, dihydroxymaloic acid, *d*-gluconic acid, hydroxyvaleric acid, hydroxypropionic acid or hydroxypivalic acid.

9. A refrigeration working fluid according to claim 7
characterised in, that
the hydroxyfunctional carboxylic acid is an α-phenylcarboxylic acid having at least two hydroxyl groups directly pendant to the phenyl ring, such as 3,5-dihydroxybenzoic acid.

10. A refrigeration working fluid according to any of the claims 1-9
characterised in, that
at least one chain extender in the dendritic or hyperbranched macromolecule is a lactone selected from the group consisting of δ-valerolactone, β-propiolactone, ε-caprolactone and glycolide.

11. A refrigeration working fluid according to any of the claims 1-10
characterised in, that
at least one chain stopper is a carboxylic acid selected from the group consisting of formic acid, acetic acid, propionic acid, isopropionic acid, butanoic acid, isobutanoic acid, valeric acid, isovaleric acid, hexanoic acid, isohexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, isooctanoic acid, nonanoic acid, isononanoic acid, decanoic acid, isodecanoic acid, acrylic acid, methacrylic acid, crotonic acid, caproic acid, caprylic acid, capric acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, lignoceric acid, cerotic acid, montanoic acid, abietic acid, sorbinic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, erucic acid, benzoic acid, *p*-tert.butylbenzoic acid, soybean fatty acid, linseed fatty acid, castor fatty acid, dehydrated castor fatty acid, tall oil fatty acid, tung oil fatty acid, sunflower fatty acid, safflower fatty acid, tallow fatty acid and oiticica fatty acid.

12. A refrigeration working fluid according to any of the claims 1-11 **characterised in**, that
at least one chain stopper is a carboxylic acid selected from the group consisting of a mono, di or trialkyl acetic acid, such as methylethylacetic acid and trimethylacetic acid; a mono, di or trialkyl propionic acid, such as 2,2-dimethylpropionic acid; a mono, di or trialkyl butanoic acid, such as 2-ethyl-2-methylbutanoic acid; a mono, di or trialkyl hexanoic acid, such as 2-methylhexanoic acid, 2-ethylhexanoic acid, 2,2-dimethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and an alkylbenzoic acid, such as *p*-tert.butylbenzoic acid.

13. A refrigeration working fluid according to claim 1 **characterised in**, that
the nucleus is a di, tri or polyfunctional carboxylic acid, or where applicable an anhydride thereof, having 3-24 carbon atoms, whereby a dendritic or hyperbranched macromolecule wherein said terminal functions substantially are carboxyl groups is yielded; and that the chain stopper is an aliphatic or cycloaliphatic alcohol or ether alcohol having 1-30, such as 10-20, carbon atoms, wherein one or more carbon atoms are alkanyl, alkenyl, alkynyl or aryl substituted.

14. A refrigeration working fluid according to claim 13 **characterised in**, that
the alcohol is a propanol, a butanol, a pentanol, a hexanol, a heptanol, an octanol, a nonanol, a dodecanol or mixtures thereof or therewith.

15. A refrigeration working fluid according to claim 13 **characterised in**, that
the alcohol is a monofunctional alcohol selected from the group consisting of 5-ethyl-1,3-dioxane-5-methanol, trimethylolpropane diallyl ether, pentaerythritol triallyl ether, lauryl alcohol, palmityl alcohol, oleyl alcohol and/or ceryl alcohol or is a mixture thereof or therewith.

16. A refrigeration working fluid according to any of the claims 13-15 **characterised in**, that
the alcohol is ethoxylated or propoxylated.

17. A refrigeration working fluid according to any of the claims 1-16 **characterised in**, that
the refrigerant comprises at least one fluoroethane selected from the group consisting of

i) a difluoroethane, such as 1,1-difluoroethane;
ii) a trifluoroethane, such as 1,1,1-trifluoroethane;
iii) a tetrafluoroethane, such as 1,1,1,2-tetrafluoroethane; and
iv) a pentafluoroethane.

18. A refrigeration working fluid according to claim 1 **characterised in**, that
the nucleus of the dendritic or hyperbranched macromolecule is a di, tri or polyfunctional alcohol having a neopentyl structure or a reaction product between such an alcohol and ethylene oxide and/or propylene oxide, whereby a dendritic or hyperbranched macromolecule wherein said terminal functions substantially are hydroxyl groups is yielded; that the chain extender is a dihydroxyfunctional monocarboxylic acid; and that the chain stopper is a linear or branched aliphatic saturated or unsaturated monocarboxylic acid having 1-24 carbon atoms.

19. A refrigeration working fluid according to claim 18 **characterised in**, that
the dihydroxyfunctional carboxylic acid is 2,2-dimethylolpropionic acid.

20. A refrigeration working fluid according to claim 18 or 19 **characterised in**, that
1-5 generations of the chain extender is added to the nucleus of the dendritic or hyperbranched macromolecule.

21. A refrigeration working fluid according to any of the claims 18-20 **characterised in**, that
the refrigerant is a tetrafluoroethane, preferably 1,1,1,2-tetrafluoroethane.

22. A refrigeration working fluid according to any of the claims 1-21 **characterised in**, that
the lubricant in addition to said dendritic or hyperbranched macromolecule comprises at least one ester of general formula
$R^1 - (R^2)_{m-n} - (R^3)_n$ wherein
R^1 is a substituted or unsubstituted alkanyl, alkenyl, alkynyl, cycloalkanyl, cycloalkenyl, cycloalkynyl or aryl group derived from an alcohol, ether alcohol or from a carboxylic acid or anhydride,
R^2 is HO or HOOC,
R^3 is $\underset{\underset{O}{\|}}{C} - R^4$ or $O - R^4$ wherein R^4 is a linear or branched alkanyl, alkenyl or alkynyl group,
and wherein *n* and *m* are integers being at least 1, whereby *m* is greater than or equal to *n* and whereby *m-n* can equals 0.

23. A refrigeration working fluid according to any of the claims 1-22 **characterised in**, that
the fluid comprises 1-60% by weight of the lubricant and 40-99% by weight of the halocarbon.

24. A lubricant composition primarily intended for refrigeration systems **characterised in**, that
the lubricant composition comprises at least one completely or partly chain terminated dendritic or hyperbranched macromolecule of anyone of Claims 1-20.

25. A lubricant composition according to claim 25 **characterised in**, that
the lubricant composition in addition to said dendritic or hyperbranched macromolecule comprises at least one ester of general formula
$R^1 - (R^2)_{m-n} - (R^3)_n$ wherein
R^1 is a substituted or unsubstituted alkanyl, alkenyl, alkynyl, cycloalkanyl, cycloalkenyl, cycloalkynyl or aryl group derived from an alcohol, ether alcohol or from a carboxylic acid or anhydride,
R^2 is HO or HOOC,

R^3 is $\overset{\overset{O}{\|}}{C} - R^4$ or $O - R^4$ wherein R^4 is a linear or branched alkanyl, alkenyl or alkynyl group;

and wherein *n* and *m* are integers being at least 1, whereby *m* is greater than or equal to *n* and whereby *m-n* can equals 0.

26. A lubricant composition according to claim 24 or 25
characterised in, that
the lubricant composition comprises 1-80%, preferably 5-50%, by weight of the dendritic or hyperbranched macromolecule.

27. A lubricant composition according to any of the claims 24-26
characterised in, that
the lubricant composition in addition to said components comprises at least one additive, such as a stabiliser, an antioxidant and/or the like.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 97/00935

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 5/04, C10M 107/32
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K, C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5202044 A (TOSHIYA HAGIHARA ET AL), 13 April 1993 (13.04.93) --	1-27
A	WO 9416028 A1 (EXXON CHEMICAL PATENTS INC.), 21 July 1994 (21.07.94) --	1-27

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 Sept 1997	29 -09- 1997
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Dagmar Järvman Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/SE 97/00935

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5202044 A	13/04/93	CA 2050987 A	13/03/92
		DE 69115185 D,T	02/05/96
		EP 0475751 A,B	18/03/92
		ES 2082148 T	16/03/96
		JP 2573111 B	22/01/97
		JP 5005098 A	14/01/93
		JP 5209171 A	20/08/93
		JP 6293893 A	21/10/94
WO 9416028 A1	21/07/94	AU 5963494 A	15/08/94
		BR 9405745 A	05/12/95
		CA 2153388 A	21/07/94
		CN 1091148 A	24/08/94
		EP 0678115 A	25/10/95
		IL 108066 D	00/00/00
		JP 8505422 T	11/06/96
		US 5494597 A	27/02/96
		ZA 9400071 A	17/08/94